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보건학석사 학위논문

A Study of the Particulate Matter  
Including Respirable Crystalline Silica,  
Carbon Monoxide and TVOCs in Some  
Pottery Workplaces

일부 도예 작업장의 호흡성 유리규산을 포함한 입자상  
물질 및 일산화탄소, 총 휘발성 유기화합물에 관한 연구

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# Abstract

## A Study of the Particulate Matter, Including Respirable Crystalline Silica, Carbon Monoxide, and TVOCs, in Some Pottery Workplaces

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**Objective:** Ceramics with raw clay and glaze are made in traditional pottery workplaces. When firing them in a kiln, particulate matter and gaseous substances that cause adverse health effects are generated. However, exposure assessment studies of the various pottery manufacturing processes or kiln types are insufficient. Therefore, this study aimed to compare the particulate matter concentrations by particle size distribution and respirable crystalline silica (RCS) generated in pottery workplaces by each kiln type and work process, and assess factors that change the concentration levels of particulate matter, monitor carbon monoxide (CO) and total volatile compounds (TVOCs) generated by each kiln type.

**Methods:** The research was conducted in small-sized pottery workshops in Korea, a college of fine art pottery studio, and an outdoor climbing kiln and included the potters working there. Personal samples for the exposure assessment were collected by measuring total suspended particulates (TSP), respirable suspended particulates (RSP), and RCS. As an area sample, TSP, RSP, RCS, particulates with 10–10,000 nm particle size distribution, CO, and TVOCs were measured for each workplace and pottery manufacturing process. TSP, RSP were analyzed by the gravimetric analysis using an electronic balance for weighing membrane filters. And filters

which collected RSP were used for evaluate RCS by fourier transform infrared spectroscopy (FT-IR). Particulates with 10–10,000 nm particle size distribution were analyzed by a scanning mobility particle sizer (SMPS) installed in parallel with the optical particle sizer (OPS). CO and TVOCs were analyzed by a photoionization detector and an indoor air quality meter (IAQ-Calc).

**Results:** The TSP's, RSP's, and RCS's geometric mean, except for background concentration, was  $146.46 \mu\text{g}/\text{m}^3$ ,  $49.10 \mu\text{g}/\text{m}^3$ , and  $1.89 \mu\text{g}/\text{m}^3$ , respectively. Among those, four personal RCS samples' concentration exceeded American conference of governmental industrial hygienists threshold limit values (ACGIH TLV), all of which were shaping and trimming procedures. Particle number concentrations (PNCs) with a diameter of 10 nm–420 nm were approximately 7.5 times higher when the peepholes were left open ( $1.61 \times 10^5$ ) than when they were closed ( $2.16 \times 10^4$ ) during mid-term firing of the electric oxidation kiln of small-sized pottery studio. In addition, the PNC (10 nm–420 nm) in the glaze dipping bench ( $5.61 \times 10^4$ ), where the glaze powder was blended with water and mixed with a drill before the unglazed bisqueware was dipped, was 8.3 times higher than that in the glaze spray booth ( $6.73 \times 10^3$ ) in glaze room of collage of fine arts studio. The CO concentration was the highest in the electric oxidation kiln (when oxidation firing), with average and maximum concentrations of 3.55 ppm and 23.7 ppm, respectively. Conversely, the TVOCs concentration was the highest in the climbing kiln (2<sup>nd</sup>–top floor), with average and maximum concentrations of 5,732.31 ppb and 12,034 ppb, respectively.

**Conclusion:** We confirmed that some particulate matter concentrations differed with the pottery manufacturing process and kiln type. The results showed that particulates including RCS, CO, and TVOCs could be exposed to potters. Indeed, whether the plugs are opened in the electric oxidation kiln, operation of exhaust vent during glaze spraying, and an time interval of adding firewood to the climbing kiln affect the concentration of various hazardous substances. Since there is a high risk of exposure to particulate matter and harmful gases during pottery manufacturing, wearing appropriate personal protective equipment for potters when shaping and trimming the clay and installing the local exhaust system near kilns or glaze spraying booths is recommended.

**Keywords:** Pottery, Kiln, Particulate matter, Respirable crystalline silica, Nanoparticles, Exposure assessment

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## 보존용 학위논문 정오표

페이지	정정 전	정정 후
p. 10	127.28 $\mu\text{g}/\text{m}^3$ , 49.10 $\mu\text{g}/\text{m}^3$ , and 1.88 $\mu\text{g}/\text{m}$	146.46 $\mu\text{g}/\text{m}^3$ , 49.10 $\mu\text{g}/\text{m}^3$ , and 1.89 $\mu\text{g}/\text{m}^3$

※ Table3의 데이터 값에 맞춰 본문(p. 10) 수치 단순 오타 정정.

# 1. Introduction

Pottery is the decorative craft of making a wide variety of products, including ornamental ware, tableware, bricks, and bowls, by making shapes using non-metallic inorganic materials such as clay and glaze and drying them at high temperatures in a kiln. According to the 2018 Ceramic Census results in Korea, the total number of ceramic companies (or studios) in Korea was 1,647, and that of workers was 4,369; more than 95% of companies were small-scale with less than 10 workers (KOCEF, 2019).

The pottery manufacturing process generally consists of grinding, mixing, and wedging raw clay (corresponding to pre-treatment), shaping and trimming, drying, glazing, firing, post-treatment, and packaging. After trimming the prepared clay is placed on the pottery wheel's center for shaping, and is dried for a certain period to remove moisture. This elevates the clay's strength and protects it from damage during the firing process. The greenware (the clay body completed up to the drying point) is loaded into the kiln for bisque firing at approximately 750–850 °C to strengthen the object and lessen water absorption so the glaze can be applied evenly. After leaving it in the kiln for a day or two and cooling it slowly, the bisqueware (the unglazed clay body that has been fired once) is removed from the kiln, and glaze is applied to the bisqueware surface, followed by a glaze firing at 1,200–1,400 °C. The glaze is a complex mixture made by mixing kaolin, feldspar, talcum, zinc oxides, calcium, aluminum, and other metallic oxides with water or a viscous organic material such as glycerin or dextrin. Glazing helps apply a thin layer on ceramic surfaces to express luster and patterns and increase the ceramics' strength.

However, harmful agents lurk underneath these artistic endeavors. Respirable crystalline silica (RCS), dust containing heavy metals, nanoparticles, musculoskeletal disorders, carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), and nitrogen dioxide (NO<sub>2</sub>) are known to be the primary dangerous agents that might arise during the pottery manufacturing process (Hirtle et al., 1998; Hernández-Serrato et al., 2003; Chen & Ramsey, 2008; Dinh et al., 2018; Kim et al., 2018; Bessa et al., 2020; Martinello 2022).

Occupational diseases, including pneumoconiosis and silicosis, which frequently occur in ceramic manufacturing workers, are closely related to RCS (Meijers et al., 1990; Calvert et al., 2003; Liao et al., 2015; Neghab et al., 2009). The International Agency for Research on Cancer (IARC) determined that there is sufficient evidence

for lung cancer when RCS is exposed to humans in respirable fractions and classified as a Group1 human carcinogen (IARC,1997).

Although documents or publications are available, including ceramic art majors and guidelines (Cuff, 1996; Shular, 1996; Stuart, 2015), and address ceramic work's hazards and risks, there are still insufficient exposure assessment research articles to back them up.

In this study, particulate matter's concentration levels, including RCS, nanoparticles, and some gaseous agents generated in pottery workshops using different kilns, were compared by kiln type and work process. This study aimed to examine strategies to minimize workers' exposure by examining the detrimental substances produced during traditional pottery manufacturing processes, including factors that affect their airborne concentrations.

## 2. Methods

### 2.1. Workplace description

Measurements were carried out at the pottery workplaces, including a small-sized pottery studio, a college of fine arts pottery studio, and an outdoor climbing kiln (labeled as A, B, and C, respectively) located in South Korea. The entire pottery manufacturing process was carried out at workplaces A and B. However, in workplace C, only glaze firing was employed for bisqueware (potteries fired just once) made using electric kilns. The three workplaces' characteristics are summarized in **Table 1**.

Workplace A is a small-sized studio located in downtown Incheon, with a size of approximately 19 m<sup>2</sup>. The main studio, which includes a pottery wheel and a glazing bench, and the kiln room, which houses the electric oxidation kiln, are separated by sliding doors. The main studio had an entrance door, and the kiln room had a window leading to the outside.

Workplace B is a building of the college of fine arts in Seoul. The experiments took place in the following places: (1) a pottery wheel studio with dozens of pottery wheels, (2) a glazing room for making, mixing, and applying glazes, (3) a kiln room with electric kilns of various sizes, and (4) a private studio for graduate students. Four fume hoods were installed side by side in the glazing room, which could not be used while making glaze or dipping bisqueware in the glaze but only to spray glaze on them. The personal studio is used for graduate students, and a blower was installed in the ceiling to blow the ceramic dust generated during the trimming process to the floor.

Workplace C is a climbing kiln with a length×width×height of 12 m×2 m×1.5 m and is located outdoors in Icheon. The kiln is made of factory bricks and fire-resistant clay that inclines at 15°. The kiln consists of 7 arch-shaped chambers and a chimney on the top floor. During early to mid-firing (9–10 h from the beginning), firewood was placed in the main chamber on the bottom floor to preheat the chamber to approximately 900 °C. Additional firewood was added through the stoke holes on each chamber's wall until the temperature was appropriately raised for each chamber (1,200–1,400 °C). **Table 2** shows information about the kiln characteristics.

**Table 1.** Characteristic summarization of three pottery workplaces in this study.

	Classification	Workplace		Pottery manufacturing process	No. of workers
		Area (m <sup>2</sup> )	Ventilation Status		
A	Small-sized pottery studio	Main room	Door	Shaping & Trimming Glazing (by dipping)	1–3
		Kiln room	Window, door	Bisque firing & Glaze firing	
B	College of fine arts pottery studios	Pottery wheel room	Windows, doors	Shaping and Trimming	15–20
		Personal studio	Blower, door	Glazing (by dipping or spraying)	
		Glaze room	Glaze spray booth, doors	Bisque firing & Glaze firing	
		Kiln room	Electric shutter doors		
C	Climbing kiln	-	Placed in outdoors	Glaze firing	3–7

**Table 2.** Characteristic summarization of kilns used for pottery firing.

Workplace	Kiln					
	Type	Fuel	Size	Firing condition	Maximum temperature (°C)	Ramp time (h)
A	Electric oxidation kiln	Electricity	0.3 m <sup>2</sup>	Oxidation	850 <sup>a</sup>	6–7
				Oxidation	1250 <sup>b</sup>	9–10
B	Electric reduction kiln	Electricity /LPG	0.6 m <sup>2</sup>	Oxidation/Reduction	1,220–1,280 <sup>b</sup>	12–14
C	Climbing kiln	Pine firewood	12 m×2 m×1.5 m (L×W×H)	Oxidation/Reduction	1,200–1,400 <sup>b</sup>	16–17

Bisque firing is also performed in B and C; it is commonly fired with an electric oxidation kiln, a type of kiln similar to that used in A.

<sup>a</sup>Bisque firing, <sup>b</sup>Glaze firing.

## **2.2. Sampling and evaluating methods**

### **2.2.1. Sampling design**

Total suspended particulates (TSP), respirable suspended particulates (RSP), and RCS were measured and analyzed for both area and personal samples. Area samples were measured from 0.8 m to 1.5 m from the floor depending on the working posture (standing or sitting). Except for Workplace C's main chamber, all area samples were measured within a 1 m radius of the working place or emission source. In Workplace C's main chamber, area samples were measured about 1.5 m away from the stoke hole because there was a risk of hitting a pump, and firewood had to be piled up.

For personal samples, the air in the worker's breathing zone's vicinity was measured only for those who wished to participate in the study. In Workplace A, it was measured when glazing, shaping, and trimming were performed in a day or when only shaping and trimming were performed in a day by one worker. In Workplace B, personal samples were collected when 3 workers only shaped or trimmed with a knife. In Workplace C, samples were collected when 4 workers put pine firewood into the climbing kiln's main chamber.

Using real-time measurements, gaseous agents such as CO and total volatile organic compounds (TVOCs) were measured along with particles for the entirety or a portion of working time. Since no gaseous substance was detected in the work where a kiln was not used, only the values measured in the kiln were presented (**Table 6**).

The Seoul National University International Review Board (IRB) approved our research ethics, as it includes personal sampling data from the potters (IRB No. 2202/001-009).



## 2.2.2 Evaluating for TSP, RSP and RCS

TSP's, RSP's, and RCS's measurement and analysis were performed according to the NIOSH Manual of Analytical Methods (NMAM) (0500, 0600, and 7602 methods).

For TSP, a 37 mm polyvinyl chloride (PVC) filter, pore size 5  $\mu\text{m}$ , diameter 37 mm, (SKC inc., USA) was installed in a 3-piece cassette (SKC 225-2LF, SKC, USA) and then connected to either of the two types of air sampling pumps (KMS-5100, KEMIK Corporation, South Korea & Escort Elf pump, MSA, USA) with a flow rate of 2 L/min. RSP was measured by attaching an aluminum cyclone to a cassette containing a 37 mm PVC filter and connecting it to an air sampling pump (GilAir Plus pump, Gillian, USA) with a 2.5 L/min flow rate.

RSP was measured by attaching an aluminum cyclone (SKC 225 2-1, SKC, USA) to a cassette containing a 37 mm PVC filter, connecting it to an air sampling pump at a 2.5 L/min flow rate. After the PVC filter was stored under a constant temperature and humidity room for more than 24 h, it was weighed three times with an electronic analytical balance (Mettler XP6, Mettler Toledo, USA), with the average calculated. All pumps were calibrated with a flow calibrator (Defender 520-M, MesaLabs, USA) before and after measurement.

To evaluate RCS, PVC filters with RSPs were placed in porcelain crucibles and incinerated in an electrical furnace at a maximum temperature of 650  $^{\circ}\text{C}$  for approximately 2 h. After that, 200 mg of KBr powder was mixed with each sample and placed in a mortar. The samples were then finely ground with a pestle and compressed, using a laboratory press to make 13 mm-sized pellets. These pellets were mounted on the FT-IR (CARY630, Agilent, USA) holder. The absorbance was analyzed at 800  $\text{cm}^{-1}$ . Using certificated NIST-SRM1878a, 6 samples ranging from 2.5  $\mu\text{g}$  to 50  $\mu\text{g}$  were prepared for the calibration curve. The correlation coefficient factor ( $r^2$ ) was 0.998 and the limit of detection (LOD), calculated by threefold standard deviations from seven black sample replicates, was 0.133  $\mu\text{g}/\text{sample}$ .

Background TSP, RSP and RCS samples were collected from the outside air of workplaces A and B, where work was carried out indoors, and workplace C, where the kiln was located outdoors, before and after firing was collected and analyzed.

### **2.2.3 Real-time measurement of particle number concentration**

To determine the size distribution of particles generated in each pottery manufacturing process, a scanning mobility particle sizer (NanoScan SMPS 3910, TSI, USA), which measures particles with 10 nm to 420 nm diameter, was installed in parallel with the optical particle sizer (OPS 3330, TSI, USA), which measures those with 0.3  $\mu\text{m}$  to 10  $\mu\text{m}$  diameter. SMPS and OPS had flow rates of 0.8 L/min and 1 L/min, respectively, with a sampling time interval of 1 min. A diffusion drier was also linked to SMPS for measurement to manage the relative humidity. Particle number concentrations (PNCs) were calculated according to the midpoint diameter ( $D_p$ ) using the aerosol instrument manager software (AIM 9.0, TSI, USA) and the Multi-Instrument Manager software (MIM 3.0, TSI, USA)

### **2.2.4 Real-time measurement of CO, TVOCs**

A photoionization detector (ppbRAE, RAE systems, Denmark) and an indoor air quality meter (IAQ-Calc 7545, TSI, USA) were used to measure CO and TVOCs emitted during kiln firing. Devices were fixed and measured in the same place as the filter sampling locations with a sampling time interval of 1 min. However, in the climbing kiln, measurements were started on the first floor, and intermittently carried out by moving the measuring instruments up one floor at a time from the stoke hole on the second floor to the one near the stoke hole on the uppermost floor (within a radius of 1 m) according to the workers' movements.

## 2.3. Statistical methods

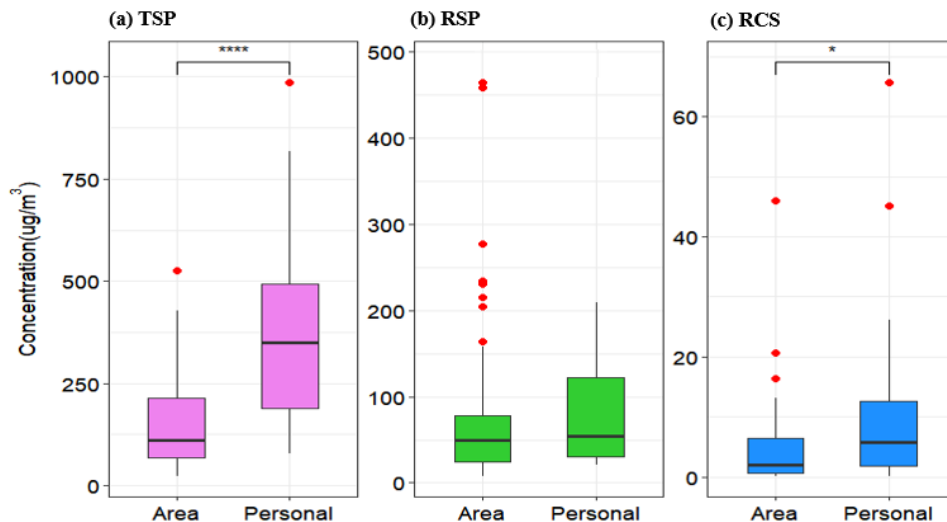
TSP, RSP, and RCS concentration values were separated per workplace A, B, and C measurement locations and summarized using geometric mean (GM), geometric standard deviation (GSD), and range (min-max). No normal distribution was found when the Shapiro–Wilk test was used to examine each analytical group's TSP, RSP, and RCS concentration values. When the data followed the log-normal distribution, a post-hoc test was performed with the Bonferroni method, including analysis of variance. The Wilcoxon rank-sum test was used to compare GM concentrations between personal and area samples, which did not follow a log-normal distribution. A value detected as less than the LOD concerning RCS was determined as 0.09  $\mu\text{g}$ , corresponding to the  $\text{LOD}/\sqrt{2}$  (Hornung & Reed, 1990). Statistical tests were performed at  $p < 0.05$  (two-tailed) with R software v.4.2.0 (R development Core Team, Vienna Austria). R software and Microsoft Excel 2016 (Microsoft Corporation, USA) were utilized for data arrangement and generating figures.

### 3. Results

#### 3.1. TSP, RSP, and RCS concentrations between study subjects

The area and personal samples' overall concentration distribution measured in three pottery workplaces is shown in **Table 3**. The TSP's, RSP's, and RCS's GM, except for background concentration, was  $127.28 \mu\text{g}/\text{m}^3$ ,  $49.10 \mu\text{g}/\text{m}^3$ , and  $1.88 \mu\text{g}/\text{m}^3$ , respectively, with a range of  $22.43\text{--}987.08 \mu\text{g}/\text{m}^3$ ,  $7.51\text{--}465.15 \mu\text{g}/\text{m}^3$ , and  $0.09\text{--}65.73 \mu\text{g}/\text{m}^3$ , respectively.

The three factors' GM concentrations between area and personal samples were compared (**Figure 1**). There was a statistically significant difference in TSP's GM concentration between area ( $118.64 \mu\text{g}/\text{m}^3$ ) and personal ( $298.60 \mu\text{g}/\text{m}^3$ ) samples ( $p < 0.001$ ). Also in RCS's GM concentration, there was a statistically significant difference between area ( $1.51 \mu\text{g}/\text{m}^3$ ) and personal ( $4.13 \mu\text{g}/\text{m}^3$ ) samples ( $p < 0.05$ ). However, there was no statistically significant difference in RSP's GM concentration between area ( $46.25 \mu\text{g}/\text{m}^3$ ) and personal ( $60.92 \mu\text{g}/\text{m}^3$ ) samples.



**Figure 1. Boxplots of TSP, RSP, and RCS concentrations by sampling type. The Wilcoxon rank sum test was performed to compare the GM concentrations. Red dots in the box plots refer to the outliers.**

\*  $p < 0.05$ , \*\*\*\*  $p < 0.001$

**Table 3.** Airborne concentration ( $\mu\text{g}/\text{m}^3$ ) of TSP, RSP and RCS in pottery manufacturing workplaces.

Sample type	TSP			RSP			RCS			
	n	GM(GSD)	Range	n	GM(GSD)	Range	n	GM(GSD)	Range	
A Area	Personal	4	220.28(2.00)	123.49-593.96	4	61.30(1.97)	34.82-164.65	4	6.64(2.17)	2.76-18.26
	Pottery wheel bench	4	188.59(1.48)	106.48-263.40	4	83.26(1.55)	55.83-125.59	4	3.38(11.58)	0.09-16.44
	Glaze dipping bench	3	93.63(1.66)	59.76-161.95	3	51.35(1.40)	35.3-67.2	3	8.22(1.58)	4.96-12.09
	Bisque firing	9	118.33(1.32)	84.99-182.45	12	43.00(1.74)	15.42-92.46	12	6.46(1.62)	2.23-12.34
	Glaze firing	9	84.55(1.64)	35.25-179.80	9	25.51(2.27)	8.09-96.43	9	3.99(1.90)	1.30-7.92
	Subtotal	29	120.89(1.74)	35.25-593.96	32	42.86(2.04)	8.09-164.65	32	5.34(2.63)	0.09-18.26
	Background	5	28.48(2.59)	12.59-126.67	5	10.39(2.33)	4.24-24.67	4	0.25(3.32)	0.09-0.74
B Area	Personal	11	295.04(1.92)	78.52-615.09	11	50.14(2.00)	20.49-138.64	11	7.55(6.47)	0.09-65.73
	Pottery wheel room	6	216.28(2.19)	48.98-422.90	6	89.91(2.87)	17.83-276.95	5	11.21(2.97)	3.14-46.03
	Glaze firing	15	95.03(2.40)	32.71-251.52	18	38.08(2.05)	9.35-144.44	18	0.74(4.66)	0.09-4.17
	Glaze dipping bench	3	100.42(1.18)	84.35-115.37	2	71.76(1.10)	66.96,76.90	2	0.09(1)	0.09
	Glaze spray booth	3	39.41(1.70)	22.43-63.95	3	14.76(1.64)	9.03-24.25	3	0.29(7.37)	0.09-2.87
	Subtotal	38	140.73(2.43)	22.43-615.09	40	44.92(2.37)	9.03-276.95	39	1.68(8.42)	0.09-65.73
	Background	4	44.44(1.33)	32.71-65.06	4	26.47(2.17)	8.55-49.54	4	0.79(5.15)	0.09-3.56
C Area	Personal	6	373.84(2.27)	119.33-987.08	6	86.69(2.21)	23.49-209.33	6	1.00(3.51)	0.09-2.69
	First floor(main chamber)	9	149.17(1.99)	61.85-345.27	10	46.05(2.84)	7.51-230.61	10	0.90(2.40)	0.09-1.73
	Top floor	10	166.64(2.88)	25.71-524.85	9	86.88(4.32)	11.47-465.15	9	0.27(3.61)	0.09-1.30
	Subtotal	25	194.39(2.53)	25.71-987.08	25	67.36(3.20)	7.51-465.15	25	0.60(3.45)	0.09-2.69
	Background	2	58.35(1.05)	56.21,60.58	2	27.71(1.75)	18.66,41.14	2	0.09(1)	0.09
<b>Total<sup>a</sup></b>	92	146.46(2.28)	22.43-987.08	97	49.10(2.50)	7.51-465.15	96	1.89(5.96)	0.09-65.73	

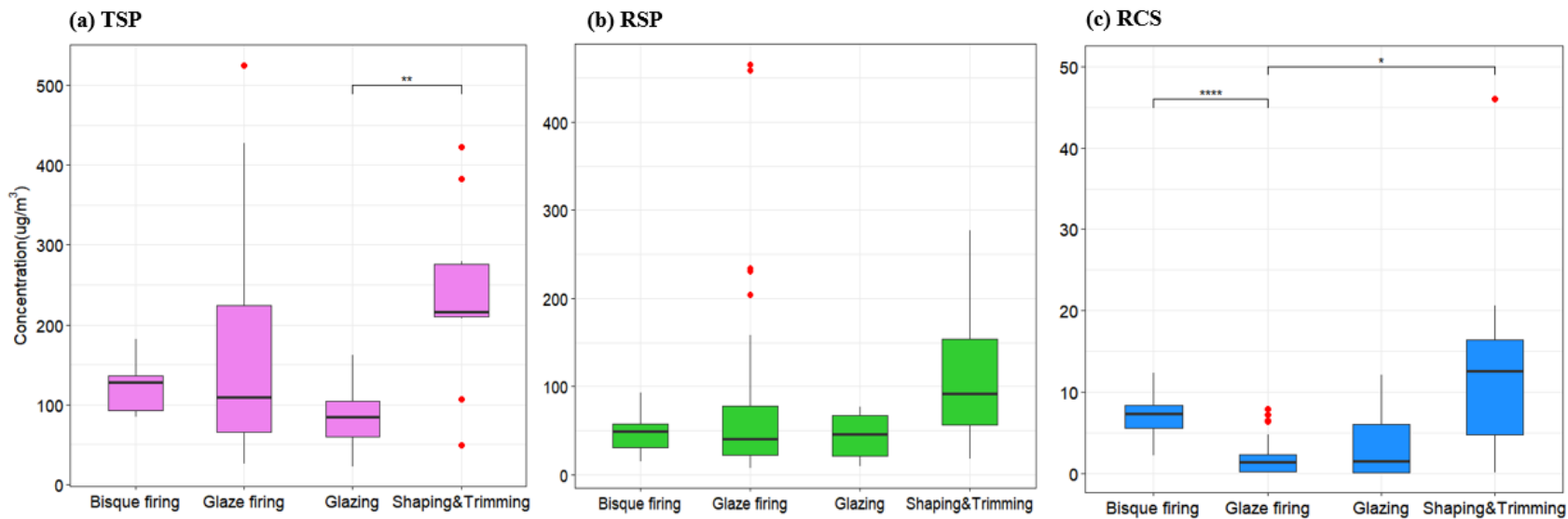
**Abbreviations:** GM, Geometric mean; GSD, Geometric standard deviation; TSP, Total suspended particulates; RSP, Respirable suspended particulates; RCS, Respirable crystalline silica

<sup>a</sup> The total value was calculated, excluding the background value.

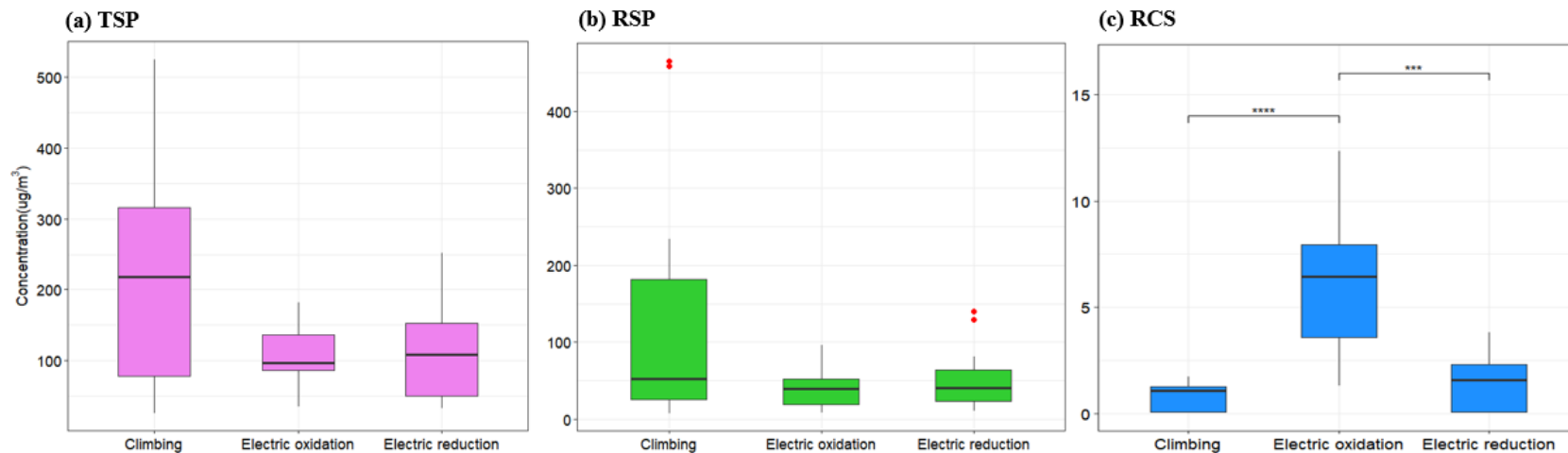
**Figure 2** is a boxplot showing TSP, RSP, and RCS concentration distributions by the pottery manufacturing process. For TSP, there was a statistically significant difference between glazing, and shaping and trimming ( $p < 0.01$ ). In RCS, there were statistically significant differences between the bisque and the glaze firing ( $p < 0.001$ ) and the shaping and trimming and the glaze firing ( $p < 0.05$ ); however, there was no statistically significant difference in GM concentration between work processes.

The RCS's GM concentrations according to the three kiln types were different in electric oxidation and climbing kilns ( $p < 0.001$ ) and in the electric oxidation and reduction kilns ( $p < 0.005$ ). However, there was no statistically significant difference between TSP and RSP (**Figure 3**).

**Table 4** shows that the total firing time for each kiln is divided into 3 or 5 periods. In the electric oxidation and reduction kilns, there was no statistically significant difference in the TSP's, RSP's, and RCS's GM concentration by firing period. However, the TSP's GM concentration in the climbing kiln's 5<sup>th</sup> period was lower than that of the 2<sup>nd</sup> and 3<sup>rd</sup> ( $p < 0.005$ ). In addition, the RSP's GM concentrations in the 1<sup>st</sup> and 5<sup>th</sup> period was lower than that of the 3<sup>rd</sup> ( $p < 0.005$ ).



**Figure 2. TSP, RSP, and RCS concentrations' boxplots by the manufacturing process. The post-hoc test with the Bonferroni method was conducted to compare the GM concentrations.**



**Figure 3. TSP, RSP, and RCS concentrations' boxplots by the kiln type. The post-hoc test with the Bonferroni method was conducted to compare the GM concentrations.**



**Table 4.** Airborne concentration ( $\mu\text{g}/\text{m}^3$ ) of TSP, RSP and RCS by sampling period

Kiln type	Firing period	Kiln temperature( $^{\circ}\text{C}$ )	TSP			RSP			RCS		
			n	GM(GSD)	Range	n	GM(GSD)	Range	n	GM(GSD)	Range
Electric oxidation	1st	330~340*, 500~520**	6	88.74(1.45)	54.35-157.81	7	28.68(2.23)	8.09-86.56	7	6.17(1.33)	3.57-8.13
	2nd	720~730*, 1,050~1,070**	6	118.66(1.32)	89.14-179.80	7	46.86(1.50)	27.86-96.43	7	5.89(1.41)	3.06-8.08
	3rd	~850*, ~1,250**	6	95.02(1.79)	35.25-182.45	7	30.22(2.33)	15.42-92.46	7	3.98(2.52)	1.30-12.34
<i>p</i> -value			> 0.05			> 0.05			> 0.05		
Electric reduction	1st	760~780	5	82.47(2.24)	32.71-251.52	6	26.77(2.01)	10.89-66.77	6	1.27(3.72)	0.09-3.56
	2nd	920~940	5	86.73(1.89)	39.36-155.70	6	29.18(1.88)	10.47-56.09	6	0.33(4.23)	0.09-1.96
	3rd	1,220~1,280	5	120.01(1.99)	44.25-230.66	6	70.67(1.93)	23.73-139.55	6	0.95(6.20)	0.09-3.83
<i>p</i> -value			> 0.05			> 0.05			> 0.05		
Climbing kiln	1st <sup>a</sup>		4	115.66(1.98)	67.35-312.99	3	53.98(1.28)	42.44-70.27	3	0.21(4.09)	0.09-1.08
	2nd <sup>b</sup>		3	263.77(1.18)	217.85-296.53	4	43.99(4.49)	7.51-234.40	4	0.24(3.09)	0.09-0.79
	3rd <sup>c</sup>	N.A.	4	348.30(1.15)	314.66-427.40	4	185.34(1.21)	158.06-230.61	4	1.21(1.42)	0.74-1.73
	4th <sup>d</sup>		4	221.41(2.26)	94.05-524.85	4	101.95(5.77)	18.14-465.15	4	0.64(3.68)	0.09-1.51
	5th <sup>e</sup>		4	47.75(1.53)	25.71-65.87	4	20.04(1.90)	11.47-37.18	4	0.69(3.85)	0.09-1.49
<i>p</i> -value			< 0.005 (0.0016)			< 0.005 (0.0019)			> 0.05		
Bonferroni post-hoc			e < b.c			a,e < c			N.A.		

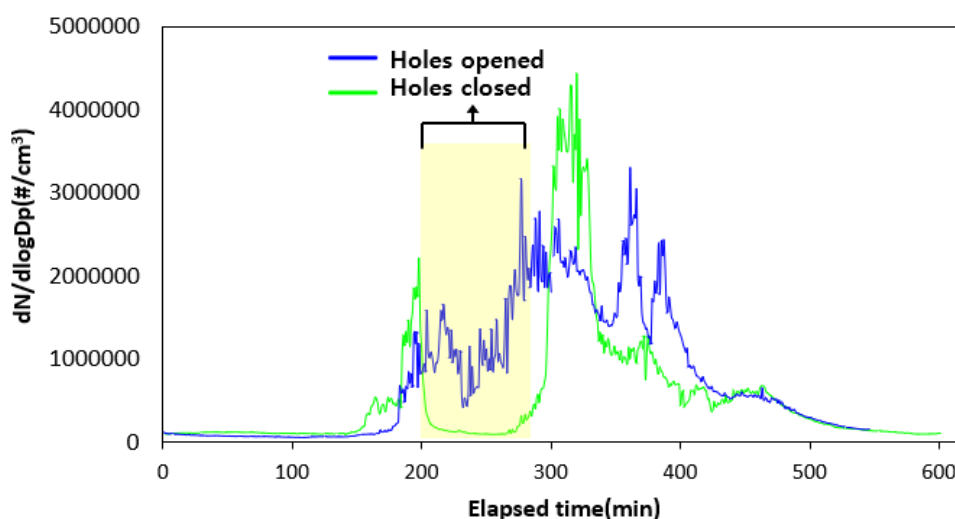
**Abbreviations:** GM, geometric mean; GSD, geometric standard deviation; TSP, total suspended particulates; RSP, respirable suspended particulates; RCS, respirable crystalline silica; N.A., not available

\*Bisque firing

\*\*Glaze firing

## 3.2. Number concentration and size distribution of particulates

The PNC levels in the three pottery manufacturing sites are summarized in **Table 5**. The data measured by SMPS were categorized into particles with 10–100 nm and 100–420 nm  $D_p$ , and the data obtained by OPS were classified into particles with 300–1,000 nm and 1,000–10,000 nm  $D_p$ . **Table 5** shows PNCs excluding background concentrations (values at the time when no work was being performed or the kiln was not operating). The reason for dichotomizing the same kiln into two rows is to compare the concentration of the two different situations: when the peephole plugs were closed from 200 min to 286 min from the time the kiln was activated (upper row), and when they were kept open for the same period (bottom row). Both experiments were carried out on the same kiln firing schedule on different days. Although there is some debate among potters, it is believed that the general firing process is to close the plugs after some amount of moisture and gas has been released (about 3 to 4 h after the kiln is operated [when kiln temperature is about 600 °C]). The PNC's difference between two situations are shown as a time graph (**Figure 4**).



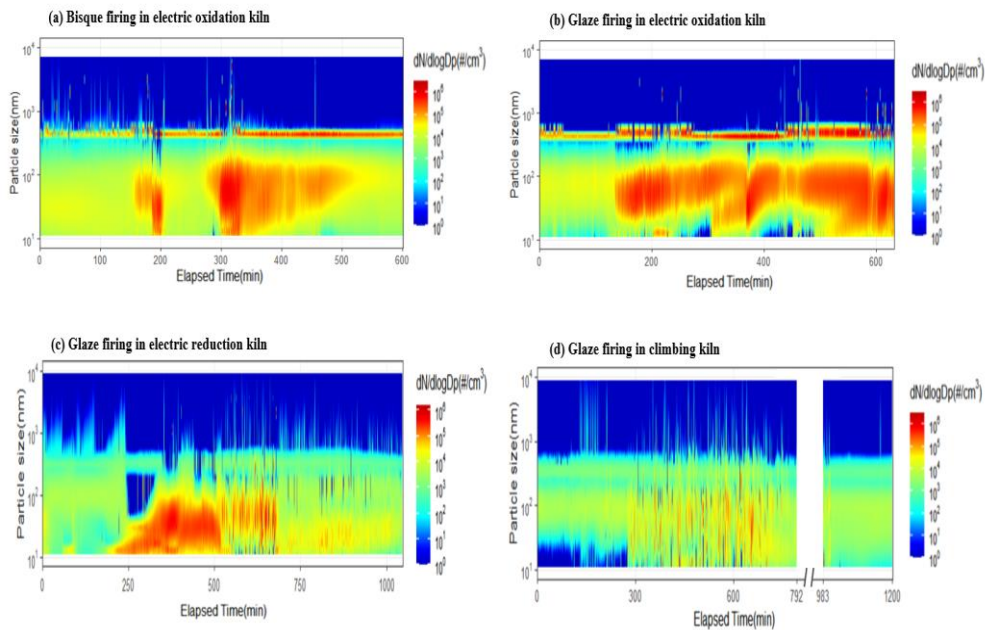
**Figure 4.** Time series of  $dN/d\log D_p (\#/cm^3)$  during the bisque firing in workplace A. The yellow background section shows differences depending on whether the plugs are opened (blue line) or closed (green line) during the bisque firing.

**Table 5.** Average PNCs (dN/dLogDp ,#/cm<sup>3</sup>) of particulates for each workplace measured by SMPS & OPS instruments.

Sampling region	Sampling time (min)	Particle Diameter				Total	
		10-100 nm	100-420 nm	300-1,000 nm	1,000-10,000 nm		
A	Pottery wheel bench	492	1.73×10 <sup>4</sup>	1.57×10 <sup>3</sup>	2.29×10 <sup>2</sup>	2.09×10 <sup>1</sup>	1.92×10 <sup>4</sup>
	Glaze dipping bench	242	1.11×10 <sup>5</sup>	2.31×10 <sup>4</sup>	1.05×10 <sup>3</sup>	1.03×10 <sup>1</sup>	3.37×10 <sup>4</sup>
	Bisque firing <sup>a</sup>	86	1.68×10 <sup>4</sup>	4.80×10 <sup>3</sup>	9.91×10 <sup>2</sup>	1.23×10 <sup>1</sup>	3.29×10 <sup>4</sup>
			1.49×10 <sup>5</sup>	1.27×10 <sup>4</sup>		N.A	
	Bisque firing	348	6.84×10 <sup>4</sup>	1.42×10 <sup>4</sup>	7.80×10 <sup>2</sup>	1.09×10 <sup>1</sup>	2.08×10 <sup>4</sup>
	Glaze firing	549	8.22×10 <sup>4</sup>	2.98×10 <sup>4</sup>	1.67×10 <sup>3</sup>	5.4	2.84×10 <sup>4</sup>
B	Pottery wheel bench	487	1.14×10 <sup>4</sup>	3.19×10 <sup>4</sup>	5.84×10 <sup>2</sup>	5.75	3.66×10 <sup>4</sup>
	Glaze firing	687	6.47×10 <sup>4</sup>	6.19×10 <sup>3</sup>	5.14×10 <sup>2</sup>	8.91	1.79×10 <sup>4</sup>
	Glaze dipping bench	722	5.15×10 <sup>4</sup>	4.62×10 <sup>3</sup>	3.56×10 <sup>2</sup>	2.55	1.41×10 <sup>4</sup>
	Glaze spray booth	239	4.59×10 <sup>3</sup>	2.15×10 <sup>3</sup>	3.42×10 <sup>2</sup>	2.92	1.77×10 <sup>3</sup>
C	First floor	792	1.64×10 <sup>4</sup>	7.53×10 <sup>3</sup>	1.98×10 <sup>3</sup>	9.23	2.59×10 <sup>4</sup>
	Top floor	801	1.71×10 <sup>4</sup>	5.16×10 <sup>3</sup>		N.A	

<sup>a</sup>The reason for dichotomizing the same kiln into two rows is to compare the concentration of the two different situations: when the peephole plugs were closed from 200 min to 286 min from the time the kiln was activated (upper row) and when they were kept open for the same period (bottom row). Both experiments were carried out on the same kiln firing schedule on different days.

**Figure 5** shows a time series of PNC ( $dN/d\text{LogDp}$ ) measured at each kiln. The particles were measured from the time the kiln started operating until the time of cooling after electricity or firewood fuel supply was stopped. In the case of the Glaze firing in climbing kiln (**Figure 5-d**), particulates could not be measured between 792 and 983 minutes due to a power supply problem. As shown in **Table 5**, The PNC's with 10nm-10,000nm particle size distribution of each kiln showed high average in the order of glaze firing in electric oxidation kiln ( $2.84 \times 10^4$ ), glaze firing in climbing kiln ( $2.59 \times 10^4$ ), bisque firing in electric oxidation kiln ( $2.08 \times 10^4$ ), and glaze firing in electric reduction kiln ( $1.79 \times 10^4$ ).



**Figure 5. Evolution graphs of particle size distribution. PNCs data from SMPS and OPS were merged by using the MIM software.**

### 3.3. Concentrations of CO and TVOCs

**Table 6** displays the CO and TVOCs concentrations near three kilns. Both gaseous substances were measured when the kiln was being operated, and their concentrations were sorted by kiln type's sampling time, average, and range. The CO concentration was the highest in the electric oxidation kiln (when oxidation firing), with both average and maximum concentrations of 3.55 ppm and 23.7 ppm, respectively. Conversely, the TVOCs concentration was the highest in the climbing kiln (2<sup>nd</sup>-top floor), with average and maximum concentrations of 5,732.31 ppb and 12,034 ppb, respectively.

**Table 6.** CO and TVOCs concentrations for each kiln type.

Firing type	Sampling time(min)	CO (ppm)		TVOCs (ppb)	
		Average	Range	Average	Range
Electric oxidation kiln (Bisque firing)	545	3.55	N.D-23.7	453.94	N.D-748
Electric oxidation kiln (Glaze firing)	602	1.12	N.D-11.2	300.76	38-521
Electric reduction kiln	774	1.09	N.D-21.6	N.D	
Climbing kiln (First floor)	303 <sup>a</sup> , 129 <sup>b</sup>	1.57	N.D-22.2	3,355.56	N.D-9,279
Climbing kiln (2nd~top floor)	327 <sup>a</sup> , 278 <sup>b</sup>	1.02	N.D-16.8	5,732.31	1,737-12,034

**Abbreviations:** CO, carbon monoxide; TVOCs, total volatile organic compounds; N.D., not detected

<sup>a</sup>Sampling time for CO

<sup>b</sup>Sampling time for TVOCs

## 4. Discussion

We measured the concentration of particulate matter containing RCS and gaseous matter of CO and TVOCs by kiln type and work process in three pottery workplaces. Of the 21 personal RCS samples, four ( $25.56\text{--}65.73 \mu\text{g}/\text{m}^3$ ) exceeded ACGIH TLV ( $25 \mu\text{g}/\text{m}^3$ ). All of these samples were taken from two workers in Workplace B. Both workers were college students with less than two years of work experience. As they were unfamiliar with the work procedure, a large amount of clay was splattered on their work clothes, and the concentration was evaluated to be relatively high.

Although no difference in RCS GM concentration was found between the groups regarding RSP, the shaping and trimming task had higher average and median concentrations than those of the other three tasks, and one sample measured in the pottery wheel room in Workplace B exceeded ACGIH TLV. This is due to the large collection of scattered particles in the sampling filter during the clay kneading, making, and shaping. In this kind of hand-handling of ceramic powder, there is a high risk of exposure to particulates (Ribalta et al., 2019).

Furthermore, when comparing the concentration differences by the kiln type, the TSP and RSP concentrations in the climbing kiln were relatively high; however, they were not statistically significant. There was a statistically significant difference in the electric oxidation kiln RCS GM concentration compared with the other two kiln types; however, no sample exceeded  $25 \mu\text{g}/\text{m}^3$ . According to a study that analyzed 11 high school ceramic classrooms, RSP's and RCS's GM concentrations were  $0.029 \text{ mg}/\text{m}^3$  and  $0.006 \text{ mg}/\text{m}^3$ , respectively, with GM values were  $0.036 \text{ mg}/\text{m}^3$  and  $0.002 \text{ mg}/\text{m}^3$ , respectively (Fech et al., 2014).

Several interesting facts were discovered by measuring PNC results by particle size. When firing in an electric oxidation kiln, the PNCs ranging from 10 nm to 420 nm were approximately 7.5 times higher when the peepholes were left open ( $1.61 \times 10^5$ ) than when they were closed ( $2.16 \times 10^4$ ) (**Figure 4, Table 5**). This result was only observed in the electric oxidation kiln. The electric kiln used in Workplace A has a sealed structure when plugs are blocked. Once the kiln is closed, there is no

room for the nanoparticles to escape, resulting in the concentration difference. It was confirmed that, during firing in an electric kiln, the PNC increased rapidly in mid-firing and then gradually decreased, consistent with the previous study (Voliotis et al., 2014). However, unlike the electric oxidation kiln in Workplace A, the two kiln types installed in the other two workplaces used fire bricks as plugs but were not completely enclosed. This is because the electric reduction kiln brick had a small circular hole in the center. In the climbing kiln, smoke escaping from the gap could be seen while firewood was added, even when the bricks were inserted into the chambers' peephole.

The first sampling period of the climbing kiln described in **Table 4** is the time when firewood starts to be put into the main chamber. The initial firing stage (about 450–600 °C) is when structural water in the clay crystal that has not been removed even by drying is mainly evaporated, and peepholes or dampers are opened (Cuff, 1996). During this period, water vapor and volatile compounds, rather than particulate matter, escape mainly from the kilns. Conversely, in the 5<sup>th</sup> period, after finally putting firewood into the chamber, the time to block the peepholes with bricks and cool the temperature was included. Since firewood addition was stopped, no more smoke was observed. For this reason, it is judged that particulate matter concentrations were relatively low. Weyant et al. (2016) noted that fluctuations in emissions were observed when fuel was added to a continuous kiln (a connected kiln where the fire is always burning and potteries are being fired and cooled at once in different parts). Corresponding to the intermittent kiln (where the potteries are fired and cooled in batches) in this study, it was seen that the PNCs fluctuated every time firewood was added at an interval of about 5 min in the climbing kiln (**Figure 5-d**).

PNCs from 10 nm to 420 nm in the glaze dipping bench ( $5.61 \times 10^4$ ), where the glaze powder was blended with water and mixed with a drill before the unglazed bisqueware was dipped, were 8.3 times higher than those in the glaze spray booth ( $6.73 \times 10^3$ ) in workplace B (**Table 5**). Installing an exhaust fan in the glaze spray booth effectively reduces the glaze concentration sprayed in the mist form. The glazing procedure, including mixing the glaze, crushing it with a drill, and sieving it, was still undertaken on the floor or on ordinary tables in the glaze room. Although

lead-containing glaze was not used in this study's workplaces, there have been many studies on health risks due to lead or other heavy metals (Fischbein et al., 1992; Hernández-Serrato et al., 2003). Therefore, paying attention to applying management measures, including ventilating or wearing personal protective equipment, is recommended when performing glazing operations.

As shown in **Figure 5**, the tendency of particle concentrations to increase a couple hours later after (electric oxidation) kiln operation and then gradually decrease after kiln operation, and the PNC in glaze firing was higher than that in bisque burning, was similar to the previous study (Voliotis et al., 2014). Voliotis et al. (2014) reported that the PNC started decreasing after ten hours of the glaze firing process, even though the kiln temperature kept rising, and it was judged that this was because the glaze and paint applied to the ceramics were depleted. However, in this study, during glaze firing, the PNC did not decrease rapidly, not only near the 549 min time point when the kiln operation stopped, but also at the cooling time point for about 80 minutes after that. The reason for this difference is presumably due to other external factors such as the difference in the amount of applied glaze, the type of kiln, or the kiln firing schedule.

According to the CO and TVOCs measurement results presented in **Table 6**, the average and maximum CO and TVOCs concentrations were highest in the bisque firing process of the electric oxidation kiln and the climbing kiln, respectively. The TVOCs in the climbing kiln was detected at a very high concentration, with an average of  $\geq 3,355$  ppb. However, the measuring devices for area sampling were placed a little further away from where the potter was working. Regarding electric kilns, the potter would often come close to the door to check the temperature inside the kiln or open and close peepholes. In addition, in the climbing kiln, the location where the potter puts firewood into the chamber was closer to the kiln than where the measuring devices were fixed. In practice, the CO and TVOCs concentrations were occasionally greater than the maximum values shown in **Table 6** when the measuring devices were brought close to the electric kiln peepholes or the smoke generated in the climbing kiln chamber. Therefore, it may be thought that the exposure level was underestimated; however, the number of times potters worked on



the climbing kiln was quite unusual (two to four times a year). Furthermore, unlike climbing kilns, electric kilns do not require the potter to be near the electric kiln at all times. However, if the electric kiln is installed in a small indoor space, the potter is at a high risk of being chronically exposed to the particles and toxic gases emitted from the kiln during daily working hours.

Ceramic companies in Korea responded by firing, on average, 56.4 times at electric kiln and 3.0 times at firewood kiln annually (KOCEF, 2019). Although hazardous substances' concentrations in the climbing kiln were high, their exposure frequency was low; therefore, it is believed that the health risk caused by the climbing kiln is relatively small. Potters using a climbing kiln worked on bisqueware in their private workplaces, including those in Workplaces A and B, directly handling clay and using an electric kiln to perform bisque firing. The most time-consuming work in the entire process was shaping and trimming. As a consequence of this study, some samples exceeded the RCS ACGIH TLV level only in the shaping and trimming, implying that exposure to RCS by potters may pose a health concern. Therefore, for artisanal potters, reducing exposure to particulate matter or gaseous agents in the indoor private workplace environment, where they spend most of their time, will be an important strategy to reduce occupational exposure.

A limitation to this study is that it cannot cover all pottery manufacturing process types and potters because the study site was limited to three and the sample size was small. A previous study reported that high CO concentrations during the forklift operation and RCS might be exposed when moving bags of raw materials (Chen & Ramsey, 2008). These two tasks were not included in this study. In addition, the workshop where we conducted the study had no exhaust fan installed near the kiln. Therefore, the effect of exhaust fan on kiln emission could not be evaluated. Nevertheless, it is worthwhile in that it is the first study to evaluate the effect of opened or closed peephole plugs or the spray booth with an exhaust fan installed on PNCs, including the change in the concentration of particulate and gaseous substances generated in the kiln over time. Further study is required to develop a comprehensive study on how variables such as differences in proficiency, detailed working schedules, and opening and closing peepholes affect the concentration of

more substances, such as heavy metals, SO<sub>2</sub>, and NO<sub>2</sub>, than those evaluated in this study.

## 5. Conclusion

This study evaluated particulate matter's airborne concentrations and exposure levels, including RCS, CO and TVOCs, from various perspectives in small-sized pottery workplaces, colleges of fine arts pottery studios, and climbing kilns and their workers.

We have confirmed differences in some particulate matter's concentration depending on the working process, kiln type, and kiln firing time. In addition, it was confirmed that the RCS exposure standard could be exceeded during shaping and trimming. Furthermore, CO and TVOCs were detected by some kilns while firing the bisqueware.

It was also discovered that the PNCs vary dramatically depending on whether the peephole plugs were opened or closed during firing in the electric oxidation kiln and whether the exhaust vent was available during glaze spraying.

Potters typically work for long periods with no concept of a "retirement age," and since there is a high risk of exposure to particulate matter and toxic gases, it is determined that appropriate personal protective equipment and a local exhaust system are recommended.

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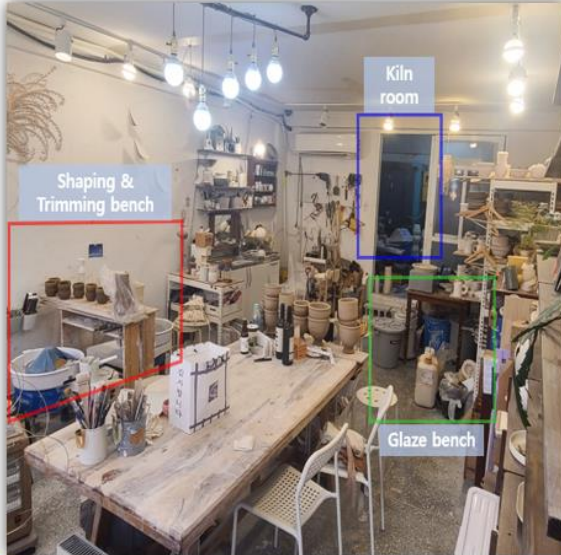
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# Appendix

## Workplace A

(a) Main room



(b) Shaping & Trimming



(c) Electric oxidation kiln



## Workplace B

(d) Glaze spraying booth



(e) Pottery wheel room



(f) Personal studio



(g) Mixing glazes



(h) Glaze dipping



(i) Electric reduction kiln



**Workplace C**

**(j) Climbing kiln (main chamber)**



**(k) Climbing kiln (2nd ~ 7th chamber)**



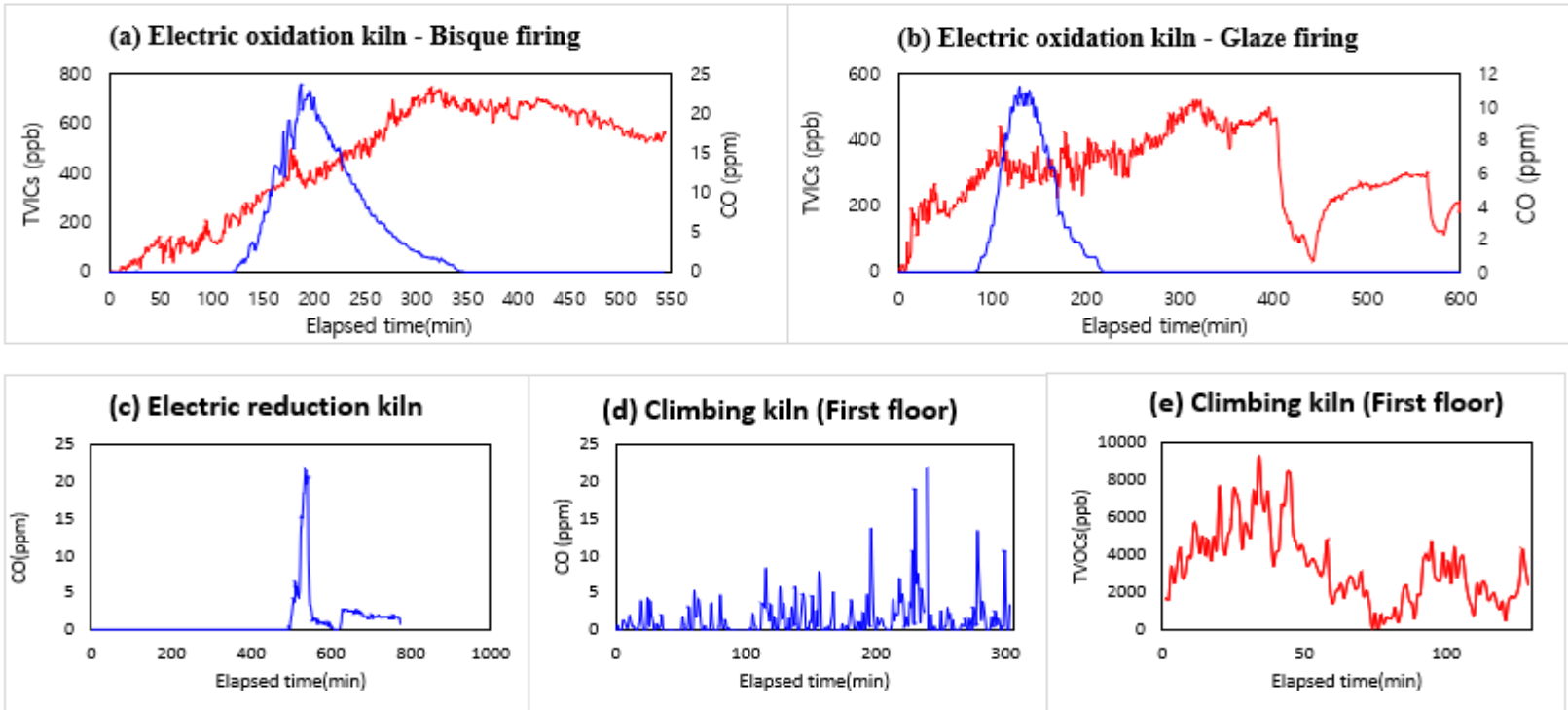
**(l) Putting firewood in to the stoke holes**

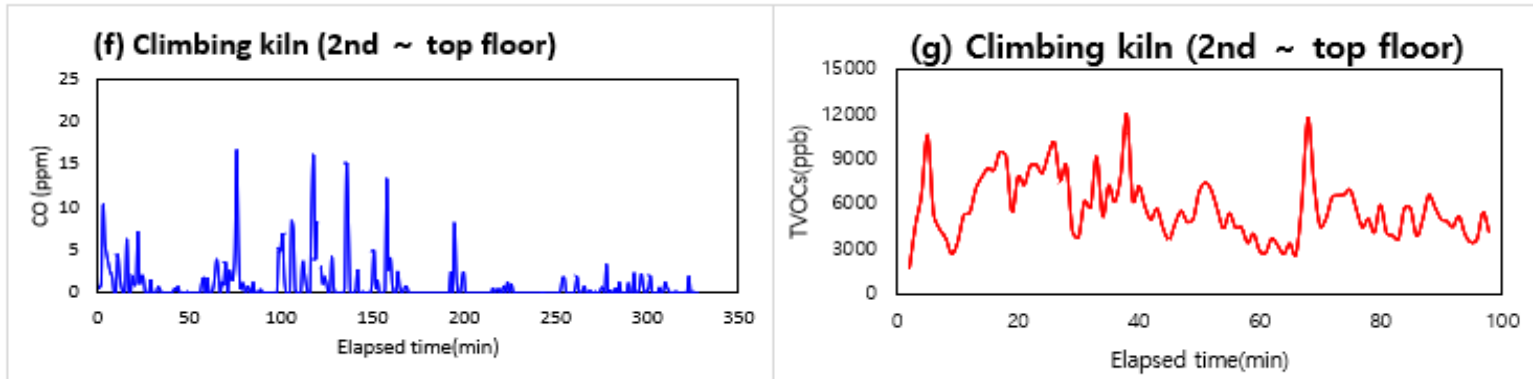


Appendix 1. Workplaces and tasks involved in this study.



— Total Volatile Organic Compounds (TVOCs)  
— Carbon Monoxide (CO)





Appendix 2. Graphs of CO and TVOCs concentrations over time by the type of the kiln.

# 국문초록

## 일부 도예 작업장의 호흡성 유리규산을 포함한 입자상 물질 및 일산화탄소, 총 휘발성 유기화합물에 관한 연구

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**연구 배경:** 전통적인 도자기를 제조하는 작업장은 원재료 점토와 유약으로 도자기를 빚고, 그것들을 가마에 소성하는 과정에서 건강상에 악영향을 미치는 입자상 물질과 가스상 물질이 발생된다. 하지만, 여러가지 작업공정과 가마 종류별로 수행된 노출평가 연구는 아직까지도 부족한 실정이다. 따라서 본 연구에서는 가마 종류별로 발생하는 일산화탄소와 총 휘발성 유기화합물(TVOCs)를 모니터링 하고, 가마 종류와 작업 공정별로 도예 작업장에서 발생하는 호흡성 유리규산을 포함하는 입경 분포별 입자상 물질의 노출 수준을 평가하는데 목적이 있다. 또한, 입자상 물질들의 노출 수준을 변화시키는 요인들도 평가하고자 한다.

**연구 방법:** 대한민국에 소재한 소규모 도예 공방, 미술대학교 공예과 실기실, 장작 오름가마와 그곳에서 작업하는 도예가들을 대상으로 연구를 수행하였다. 개인시료는 총분진과 호흡성 분진, 그리고 호흡성 유리규산을 측정하여 분석하였다. 지역 시료로는 각각의 작업 장소와 가마 근처에서, 총분진과 호흡성 분진, 호흡성 유리규산,

10nm~10,000nm의 입경분포를 지닌 입자상 물질, 일산화탄소, TVOCs를 측정하였다. 총분진, 호흡성 분진은 전자 저울을 사용하여 여과지를 중량 하였다. 그리고 호흡성 분진을 포집한 필터는 푸리에 변환 적외선 분광법(FT-IR)를 활용하여 호흡성 유리규산 분석에 사용되었다. 10-10,000 nm 입자 크기 분포를 갖는 입자는 광학 입자 계수기(OPS)와 병렬로 설치된 나노 에어로졸 입경분포 측정기(SMPS)에 의해 분석되었다. 일산화탄소 및 TVOCs는 광이온화 감지기와 실내 공기질 측정기(IAQ-Calc)로 분석되었다.

**연구 결과:** 세 곳의 도예 작업실에서 측정한 총분진, 호흡성분진, 호흡성 유리규산의 기하평균은  $146.46 \mu\text{g}/\text{m}^3$ ,  $49.10 \mu\text{g}/\text{m}^3$ ,  $1.89 \mu\text{g}/\text{m}^3$  이었다. 그 중 4개의 호흡성 유리규산 개인시료의 농도는 ACGIH TLV을 초과했으며, 4개 시료 모두 성형&정형 작업이었다. 소규모 도자기 공방의 전기가마에서 10 nm-420 nm의 직경을 갖는 입자 수농도는 초벌 소성 중기 동안 수분 배출구가 열려 있을 때( $1.61 \times 10^5$ )가 닫혀있을 때( $2.16 \times 10^4$ )보다 약 7.5배 더 높았다. 미술대 도예과에서는, 유약 분말을 물과 섞고 드릴로 혼합하는 장소인 유약 벤치( $5.61 \times 10^4$ )에서의 입자 수농도(10 nm-420 nm)가 유약 스프레이 부스 ( $6.73 \times 10^3$ )의 입자 수농도 보다 약 8.3배 높았다. 일산화탄소 농도는 전기산화(초벌 소성)에서 평균과 최고농도 모두 각각 3.55 ppm, 23.7 ppm으로 가장 높았다. 반면에, TVOCs 농도는 장작 가마(2층 ~ 최고층)에서 평균과 최고농도 모두 각각 5,732.31 ppb, 12,034 ppb로 가장 높게 나타났다.

**결론:** 본 연구를 통해 도자기 제조 공정과 가마 종류별로 일부 입자상 물질의 농도에서 차이가 있는 것과, 호흡성 유리규산을 포함한 입자상 물질, 일산화탄소 및 TVOCs가 도예가에게 노출될 수 있음을 확인하였다. 실제로 전기산화가마의 수분배출구 개방 여부, 유약 스프레이 시 국소배기의 작동, 가마에 장작을 넣는 시간 간격 등이 각종 유해물질 농도에 영향을 미칠 수 있음을 확인하였다. 이처럼, 도예 작업

시 입자상 물질 및 유해 가스 등에 노출될 위험성이 높은 바, 적절한 호흡 보호구의 착용과 국소배기장치의 설치가 권장된다.

**주요어:** 도자기, 가마, 분진, 호흡성 유리규산, 나노입자, 노출평가

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